Carbonation of Sodium Carbonate and Calcination of Sodium Bicarbonate

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Abstract

Sodium carbonate has been employed for a chemical absorption method to capture carbon dioxide from the mixture of carbon dioxide, nitrogen, and moisture. Sodium carbonate reacts with both carbon dioxide and moisture to form sodium bicarbonate by the carbonation, followed by the calcinations of sodium bicarbonate to release carbon dioxide on flushing with nitrogen to shift the reaction in reverse. A fixed bed was used to observe the breakthrough curves of carbon dioxide, which were used to obtain the reaction rate constants (carbonation rate constant and calcination rate constant) of both reactions from comparison of experimental values with simulated values. Dependence of the reaction rate constants on the reaction temperature was observed using the Arrhenius plots.

1. INTRODUCTION

Carbon dioxide is a greenhouse gas that has been emitted to the environment during the usage of fossil fuels, including electric power generation. With the projected increase in consumption and demand for fossil fuels, CO₂ emissions will correspondingly increase in the absence of any capture/sequestration strategy. In view that CO₂ is a greenhouse gas with the potential to contribute to global climate warming, existing and improved technologies to mitigate the release of CO₂ to the environment are being considered as a prudent precaution against global warming.

Carbon dioxide can be removed from flue gas and waste gas streams produced from carbon usage by various methods, those include absorption with a solvent, membrane separation, cryogenic fractionation, and adsorption using molecular sieves. Capture of CO₂ from each of these processes is costly. Another technique for removal of CO₂ is dry scrubbing or chemical absorption of CO₂ with a solid sorbent. The development of dry, regenerable scrubbing processes for CO₂ capture is the focus of the current study.

The objective of this study is to obtain the chemical kinetics of chemical absorption and/or desorption of CO₂ with solid sorbents. Specifically, sodium carbonate and sodium bicarbonate are the subjects of the experimental investigations. The chemical reaction of CO₂ capture and release using those compounds are shown in reaction (1).
\[
Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3
\]

(1)

The forward reaction path depicts absorption of CO$_2$, where the regeneration is expressed as reverse reaction path.

The breakthrough curves of CO$_2$ produced from a fixed bed, which consists of Na$_2$CO$_3$ in the forward reaction of (1), or NaHCO$_3$ in the reverse reaction path were used to get the forward or backward reaction rate constant, respectively.

**EXPERIMENTAL**

**Carbon dioxide recovery and release apparatus and its operation**

A schematic flow diagram of the apparatus employed in this study is shown in Fig. 1. The sorbent, Na$_2$CO$_3$ of 56 g was packed in a column with 20 mm in insider diameter and 200 mm in length. A thermocouple was inserted in the column center to measure the temperature of the sorbent. Moist(saturated water vapor at the reaction temperature), 12\% of CO$_2$ in gaseous stream of N$_2$ with a constant flow rate(10, 15, 20 mL/min) for the carbonation process and only N$_2$ for calcinations process were supplied from the bottom of the column at a fixed temperature, then gas flow rate and CO$_2$ concentration at the top at the column were measured by the mass-flow meter and a gas chromatography(FID), respectively. The temperature ranges for the carbonation were between 50 and 70°C, those for the calcinations, between 90 and 110°C.

![Schematic flow diagram of a fixed bed apparatus](image)

Fig. 1. Schematic flow diagram of a fixed bed apparatus.

**Physicochemical properties of sorbent and apparatus**

To get the reaction rate constants in reaction path (1) using the breakthrough curves and simulation of CO$_2$, it is necessary to know the physicochemical properties such as diffusivities of CO$_2$, moist and N$_2$, mass transfer coefficient of CO$_2$ in gas phase, and diameters of solid Na$_2$CO$_3$ and NaHCO$_3$, and porosity of the fixed bed, et al. The diameters and densities of solid Na$_2$CO$_3$ and NaHCO$_3$ were measured using sieve analyzer, and their values were 415.42 and 401.67 μm, respectively, and their densities, 2532 and 2159 kg/m$^3$, respectively. The porosity of the fixed bed filled with dry sorbent was measured as 0.54. The diffusivity of the gas was calculated by the
Hirschfelder-Bird-Spotz method[1]. The gas-side mass transfer coefficient of \( \text{CO}_2 \) was estimated by the following equation, which is used through fixed beds of pellets[2].

RESULTS AND DISCUSSION

Breakthrough curve of \( \text{CO}_2 \) for carbonation

Figure 2 illustrates the S-shaped \( \text{CO}_2 \) breakthrough curves at different flow rates of gaseous stream at carbonation temperature of 60°C as a typical temperature.

![Graph showing breakthrough curves of \( \text{CO}_2 \) for carbonation](image)

The symbols such as triangle, square and circle represent the experimental data, and the dotted, fine dotted and solid line, the values estimated from the simulation of \( \text{CO}_2 \) conservation balance. As shown in Fig. 2, the simulated values approach to the experimental ones very well, from which the average value of the forward reaction rate constant \( k_s \) in Eq. (1) was \( 2.447 \times 10^{-3} \text{ m}^4/\text{kmol.min} \). Identically, the values of \( k_s \) at the carbonation temperatures of 50 and 70°C were \( 1.786 \times 10^{-3} \) and \( 2.429 \times 10^{-3} \text{ m}^4/\text{kmol.min} \), respectively. Figure 3 shows the Arrhenius plots of \( k_s \) against carbonation temperature. As shown in Fig. 3, the plots are linear, from which the empirical equation is obtained as follows:

\[
k_s = 0.387 \exp(-3.420 \times 10^5/RT)
\]

Fig.2. Breakthrough curves of \( \text{CO}_2 \) in carbonation of \( \text{Na}_2\text{CO}_3 \). \( T=60^\circ \text{C}, \ Z=15\text{cm}, \ dp = 415.42\mu\text{m}, \ \epsilon \) =0.54, \( \rho =2532\text{kg/m}^3, \ D_{\text{Am}} =1.127 \times 10^{-3} \text{m}^2/\text{min}, \ k_s =2.447 \times 10^{-3} \text{ m}^4/\text{kmol.min} \)

Fig.3. Arrhenius plot of \( k_s \) against \( 1/T \) for carbonation of \( \text{Na}_2\text{CO}_3 \) with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

Breakthrough curve of \( \text{CO}_2 \) for calcination

Figure 4 illustrates the \( \text{CO}_2 \) breakthrough curves at different calcinations temperatures of gaseous \( \text{N}_2 \) stream. The symbols such as triangle, square and circle represent the experimental data, and the dotted, fine dotted and solid line, the values estimated from the simulation of \( \text{CO}_2 \) conservation balance. As shown in Fig. 4, the
simulated values approach to the experimental ones very well, from which the values of the backward reaction rate constant ($k_d$) in Eq. (1) at temperatures of 90, 100, and 110°C were 2.685x10^{-8}, 1.704x10^{-7}, 3.815x10^{-7} kmol/m²min, respectively. Figure 5 shows the Arrhenius plots of $k_d$ against carbonation temperature. As shown in Fig. 5, the plots are linear, from which the empirical equation is obtained as follows:

$$k_d = 4.333 \times 10^{14} \exp(-3.677 \times 10^4/RT)$$

Fig. 4. Effect of reaction temperature on CO₂ concentration at outlet in calcination of NaHCO₃, (Z =15cm, Q=10cm³/min, dp=401.67μm, ε=0.54, ρ=2159 kg/m³)

Fig. 5. Arrhenius plot of $k_d$ against 1/T for calcination of NaHCO₃.

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REFERENCES